

Experimental Optimization of Process for the Thermo-catalytic Degradation of Waste Polypropylene to Liquid Fuel

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Abstract

Waste polypropylene was cracked thermally and catalytically in the presence of kaolin clay in a batch reactor in the temperature range 400-550°C in order to obtain suitable liquid fuels. The dependencies of process temperature, effect of catalyst, feed composition on yield of the fuel fraction were determined. It was observed that up to 450°C, the major product of thermal pyrolysis was liquid oil and the major products at other higher temperatures (475-550°C) are either viscous liquid or wax. The highest yield of pyrolysis liquid product was 82.85% by weight at 500°C. Use of kaolin as catalyst decreased the reaction time and increased the yield of liquid fraction. Again, the major pyrolysis product in catalytic pyrolysis i.e. the liquid fraction at all the temperature was low viscous liquid oil. The maximum oil yield using kaolin to plastic ratio 1:3 was 87.5% at 500°C. The oil obtained in this process was analyzed using FTIR and GC-MS for its composition. Fuel properties of the oil studied by IS methods are identical with the different petro fuels. On the basis of the obtained results, hypothetical continuous process of waste polypropylene plastics processing for engine fuel production can be presented.

Keywords

Waste Polypropylene; Pyrolysis; Kaolin; FTIR; GC-MS; Engine Fuel

Introduction

Plastic waste disposal has been identified as worldwide environmental problem. In recent years, attention has been paid more towards the recycling of synthetic polymer waste for solving pollution problems and the reuse of cheap and abundant waste products. Though several methods have been proposed for recycling waste plastics, it is generally accepted that material recovery is not an ideal solution

to the present problem, and that energy or chemical recovery is a more attractive one. In this method, the waste plastics are thermally or catalytically degraded into gases and oils, which can be used as resources for fuels or chemicals. Catalytic degradation of polyolefins to oil has been preferred over thermal pyrolysis due to narrow product distribution, high reaction rate and lower temperature of degradation. One of the most commonly used solid catalysts in polymer degradation studies are zeolites due to their strong acidity, pore size and specific pore structure effects. Amongst the numerous kinds of zeolites investigated in polyolefin pyrolysis, the most commonly used are Beta, USY, ZSM-11, REY, Mordenite, ZSM-5 etc. Some other solid acid catalysts used for plastic pyrolysis include molecular sieves, silica alumina, and MCM-41. Reports on the use of FCC catalysts are also found in literature. Other catalytic materials such as clays (montmorillonite, saponite), reforming catalysts, activated carbon, metal oxides, metal complexes of the type MCl_n-AlCl_3 or $M(AlCl_4)_n$ ($M=Li, Na, K, Mg, Ca, Ba; n=1-2$), and alkali metal carbonates or alkaline metal carbonates have also been tested for polymer degradation [Panda, Singh and Mishra, 2010].

A number of laboratory studies have been conducted for the direct catalytic cracking of different type of plastics. A large variety of catalysts hasbeen used, even if wellperformed, many of them can be unrealistic from the point of view of practical use due to the cost of manufacturing and the high sensitivity of the process.

Ali Durmus et al. investigated the thermal degradation of polypropylene powder by thermogravimetric analysis (TGA) employing four different heating rates

over different type of zeolite catalysts such as BEA, ZSM-5 and MOR with different surface areas, pore structures, acidities and Si/Al molar ratios and calculated the apparent activation energies of the processes by the Kissinger equation [Durmus, NaciKoc, Selda, Pozan, and Kasgoz, 2005]. The performance of several differently treated clinoptilolite zeolites (dealuminated clinoptilolite catalysts) in the degradation of polypropylene was investigated in a semi-batch reactor at 400°C [Kim, Kim, Yoon, Park, and Woo, 2002]. The effects of different zeolites as H-Y, Na-Y, H-mordenite and Na-mordenite on the catalytic degradation of polypropylene was studied using thermogravimetry under nitrogen flow [Zhao, Hasegawa, Fujita, Yoshii, Sasaki, and Makuuchi, 1996]. The catalytic cracking of polypropylene was carried out by silica-alumina and H-ZSM-5 at temperatures between 350°C and 420°C and sulfated zirconia at temperatures below 300°C, and also by means of thermogravimetry under helium flow [Negelein, Lin and White, 1998]. The catalytic degradation of polypropylene under vacuum in a semi batch reactor, using catalysts as Al₂O₃, SiO₂, SiO₂-Al₂O₃, and Na-Y, H-Y and REY zeolites, at temperatures between 200°C and 600°C was reported [Audisio, Silvani, Beltrame, and Carniti, 1884]. Meanwhile, Sakata et al. studied the catalytic cracking of polypropylene with silica-alumina catalyst at 380°C in a semi batch reactor without external gas flow [Sakata, Uddin, Koizumi, and Murata, 1996]. Ishihara et al. investigated the catalytic degradation of polypropylene by silica-alumina at temperatures between 180°C and 300°C in a semi batch reactor under a nitrogen flow [Ishihara, Nanbu, Iwata, Ikemura, and Takesue, 1989].

Aguado et al. have studied the catalytic cracking of LDPE, HDPE and polypropylene in a semi batch reactor at 400°C under a nitrogen flow using MCM-41, H-ZSM-5 zeolite and silica-alumina as solid acid catalysts [Aguado, Serrano, Romero, and Escola, 1996, Aguado, Sotelo, Serrano, Calles and Escola, 1997]. Lin et al. have investigated the catalytic cracking of HDPE and polypropylene in a fluidized bed reactor using H-ZSM-5, H-USY, H-mordenite, silica-alumina and MCM-41, with nitrogen as fluidizing gas [Lin, Sharratt, Garforth, and Dwyer, 1998]. Mordi et al. have reported the catalytic degradation of LDPE and PP at 350°C in a batch reactor under vacuum, using zeolite catalysts as H-ZSM-5, H-Theta-1 and H-mordenite [Mordi, Fields, and Dwyer, 1994, Mordi, Fields, and Dwyer, 1992]. Uddin et al. have studied the catalytic cracking of PE and PP at 430°C and 380°C with silica-alumina, H-ZSM-5, silicalite and a non-acidic

mesoporous silica catalyst (FSM) in a semi batch reactor without external gas flow [Uddin, Koizumi, Murata, and Sakata, 1997, Uddin, Sakata, Muto, Shiragam, Koizumi and Kanada, 1998]. Catalytic cracking of polypropylene has been carried out in a semi batch stirred reactor using spent equilibrium catalyst from FCC units, large pore zeolites as well as amorphous and ordered silica-alumina in order to study extensively the influence of pore size (micro and meso), crystallite size and the number and strength of the active acid sites [Salvador, Cardona and Corma, 2000].

Lin et al. used a laboratory catalytic fluidised-bed reactor to obtain a range of volatile hydrocarbons by degradation of polypropylene in the temperature range 290-430°C using different zeolitic and non zeolitic catalysts such as HZSM-5, HMOR and HUSY, MCM-41 and SAHA and found product streams varied markedly depending on catalysts type and structure [Lin and Yen, 2005]. The thermogravimetric study of the thermal and catalytic decomposition (with MCM-41, ZSM-5 and an FCC as a catalyst) of polypropylene showed that the addition of MCM-41 produced a remarkable decrease of almost 110°C in the temperature of maximum decomposition rate [Marcilla, Go'mez, Reyes-Labarta and Giner, 2003]. Zhao et al. found that the degradation temperature of polypropylene strongly depended on the type of zeolite used and the amount added and one type of HY zeolite (320HOA) was shown to be a very effective catalyst [Zhao, Hasegawa, Fujita, Yoshii and Sasaki, 1996]. The catalytic degradation of polypropylene has been investigated using solid acid catalysts, such as silica-alumina and zeolites (HZSM-5, natural zeolite, Mordenite etc.), in the range of 350-450°C [Hwang, Choi, Kim, Park and Woo, 1998].

Achilias et al. carried out the catalytic pyrolysis of low-density polyethylene (LDPE), high-density polyethylene (HDPE) and polypropylene (PP) in a laboratory fixed bed reactor with an FCC catalyst [Achilias, Roupakias, Megalokonomos, Lappas and Antonakou, 2007].

Pyrolysis of polyolefin wastes (PP and PE fractions) was carried out in a fluidized bed reactor equipped with a char removal system, under various reaction conditions (temperature, feed rate, and fluidizing medium) [Jung, Cho, Kang and Kim, 2010].

Degradations of polypropylene (PP) and polyethylene (PE) over pure hexagonal mesoporous silica and aluminum-containing hexagonal mesoporous silica catalysts were studied in a fixed bed catalytic reactor

at 380 and 430°C, respectively [Chaianansutcharit, Katsutath, Chaisuwan, Bhaskar, Nigo and Muto, 2007].

From the extensive literature survey, it is observed that the suitability of all the catalysts used by different researchers are due to their surface structure and acidity. In addition, kaolin has not been used so far as catalyst, in the plastic pyrolysis process.

Kaolin, a clay material, is thermally stable and has some acidity, which would support cracking reactions at high temperature. Again, the cost of the material is also comparatively lower as compared to that of other catalysts used in this process. In addition, a study on the comparison of catalytic activity of the kaolin with silica alumina in the degradation of virgin polypropylene sample was carried out by us. Kaolin is found suitable for plastic degradation although not as efficient as silica alumina [Panda and Singh, 2011]. So in the present work, studies have been carried out for the thermal and catalytic degradation of waste polypropylene in batch reactor using kaolin as catalyst. Emphasis has been on the study of the performance of kaolin on the yield of liquid product and total reaction time with a view to optimizing the yield of liquid fraction of the reaction. The reusability of the kaolin was also studied in this work.

Experimental

Materials

Waste Polypropylene (used plastic disposable glasses) was collected from the waste yards of National Institute of Technology Rourkela. The waste plastic disposable glasses were cut into flakes by a shredder. Thermogravimetric analysis of the sample was carried out with a SHIMADZU DTG-60/60H instrument. A known weight of the sample was heated in a silica crucible at a constant heating rate of 10°C/min operating from 35°C to 600 °C.

The catalyst employed in this study, commercial grade kaolin clay (Composition: SiO₂ 43.12%, Al₂O₃ 46.07%, Fe₂O₃ nil, MgO 0.027%, CaO 0.030%, ZnO 0.0064%, K₂O 0.01%, TiO₂ 0.74, LOI at 1000°C 9.9%, BET surface area: 23m²/g, ammonia TPD acidity: 0.049mmol/g with mesoporous surface) was procured from Chemtex Corporation, Kolkata, India [Panda, Mishra, Mishra and Singh, 2010]

Experimental Set up and Procedure

The experimental setup used in this work consists of a batch reactor made of stainless steel (SS) tube (length-145 mm,



FIG. 1a EXPERIMENTAL SET UP AND SS TUBE

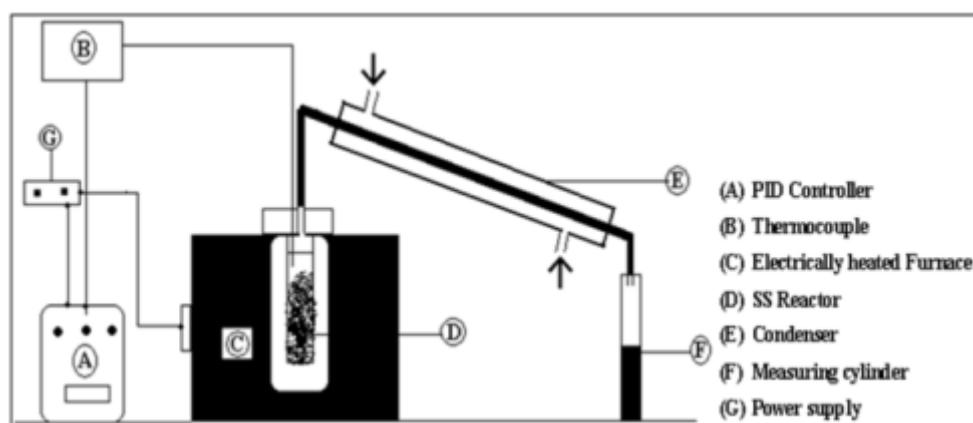


FIG. 1b SCHEMATIC REPRESENTATION EXPERIMENTAL SET UP

internal diameter- 37 mm and outer diameter- 41 mm) sealed at one end and an outlet tube at other end Figure 1 a and 1 b. The SS tube is heated externally by an electric furnace, with the temperature measured by a Cr-Al: K type thermocouple fixed inside the reactor and the temperature is controlled by external PID controller. Shimaden PID controller SR1 was used to control the temperature of the furnace. The accuracy of this PID controller is $\pm 0.3\%$ FS (FS = 1200°C). So the temperature can be measured at $\pm 3.6^\circ\text{C}$.

20g of waste polypropylene samples (disposable glass flakes) were loaded in each pyrolysis reaction. In the catalytic pyrolysis, a mixture of catalyst and the plastics in different catalyst to plastics proportion (1:2, 1:3, 1:4, 1:6, 1:10, 1:20, 1:40) was subjected to pyrolysis in the reactor set up and heated at a rate of 20°C/min. up to the desired temperature. The condensable liquid products were collected through the condenser and weighed. After pyrolysis, the solid residue left out inside the reactor was weighed. Then the weight of gaseous product was calculated from the material balance. Reactions were carried out at different temperatures ranging from 400-550°C. The reaction time was calculated from the start of reaction (when the feed was taken in the reactor and temperature raised from the room temperature) till the completion of reaction (the time when no more oil comes through outlet tube).

Analysis Methods

Thermogravimetric analyses of the samples were carried out with a SHIMADZU DTG-60/60H instrument. A known weight of the sample was heated in a silica crucible at a constant heating rate of 10°C/min operating in a stream of air with a flow rate of 40ml/min from 35°C to 600°C. Nitrogen adsorption-desorption measurements (BET method) were performed at liquid nitrogen temperature with an autosorb BET apparatus from Quantachrome Corporation. The acid properties of the catalysts were probed by ammonia TPD measurements in Micromeritics 2900 TPD equipment. FTIR spectra were recorded on a Perkin-Elmer infrared spectrophotometer as with resolution of 4 cm⁻¹, in the range of 400-4000 cm⁻¹. The components of liquid product were analyzed using GC-MS-QP 2010 [SHIMADZU] using flame ionization detector. All the fuel properties of the oil were tested by prescribed IS methods. Precision balance of SHINKODENSHI Co. LTD, JAPAN, Model: DJ 300S was used to measure the weight of the samples. This machine capacity is 200 gram and accuracy is 0.0001 gram and so the weight can be measured within $\pm 0.0001\text{g}$.

Results and Discussion

TGA of Polypropylene Sample

The thermal degradation of polypropylene samples was carried out using TGA in order to know the thermal properties. Figure 2 shows the normalized weight loss for both the samples as a function of temperature. The degradation of waste polypropylene occurred between 220°C to 440°C and the weight loss of 50% (T50) takes place at 382°C.

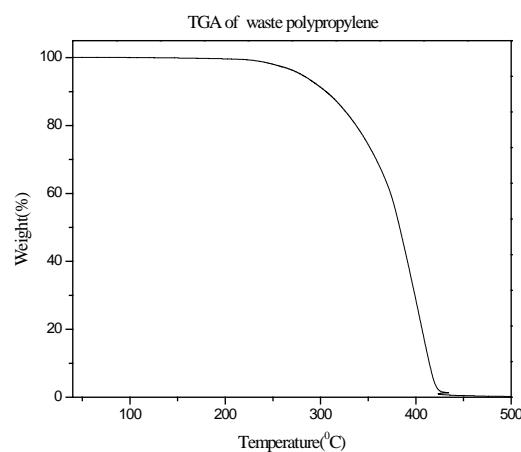


FIG. 2 TGA OF POLYPROPYLENE SAMPLES

Results of Pyrolysis

1) Effect of Temperature on Product Distribution in Thermal Pyrolysis

Three different fractions namely condensable low viscous liquid/high viscous liquid/wax like product, non condensable gases/volatiles and solid residue were obtained during pyrolysis. At different temperatures, the yield distribution of different fractions clearly differed and is summarized in figure 3. The condensable fraction (oil/wax) obtained at low temperature (400 and 450°C) was less viscous and highly volatile oil, as that obtained above 475°C were viscous liquid or wax. The recovery of condensable fraction was low (59.2wt.%) at 400°C and increased to the highest yield of 82.25 wt.% at 500°C and then gradually decreased with further increase in temperature. The vapour/volatile fractions increased at high and low temperatures leading to low condensable. At low temperature, the reaction time was more (figure 5a), due to that secondary cracking of the pyrolysis product occurred inside the reactor and resulted in large amount of highly volatile/gaseous product. Similarly, the low liquid and high gaseous yield at higher temperature was due to the formation of more non condensable gaseous/volatile fractions by rigorous cracking.

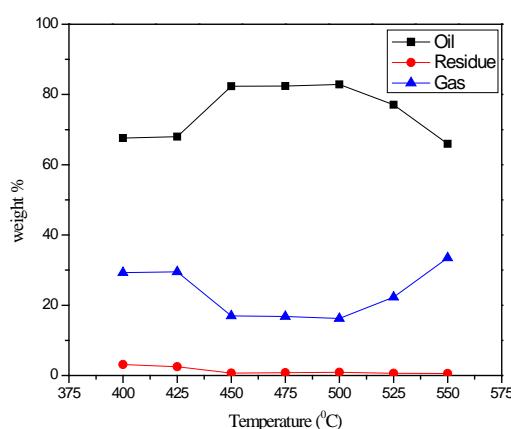


FIG. 3 EFFECT OF TEMPERATURE ON PRODUCT DISTRIBUTION OF WASTE POLYPROPYLENE

2) Effect of catalyst

The thermal decomposition of polypropylene was carried out in presence of kaolin as catalyst with different polypropylene to catalyst ratio. Reaction time decreased and oil yield increased with increment in catalyst amount (Figure 4a). The highest yield of oil (87 wt.%) was obtained at the ratio of plastics to catalyst 3:1 at 500°C. The effect of catalyst was not significant at the ratio of polymer to catalyst 20:1 and it is almost negligible at 40:1. Figure 4b shows the effect of presence of catalyst on oil yield at different temperatures. It is observed that the oil yield increased in catalytic pyrolysis compared to thermal reaction. Again, unlike in thermal pyrolysis, the condensable products in catalytic pyrolysis, even at higher temperature are also low viscous liquid and not high viscous liquid or in wax form. All the above changes in the reaction in presence of kaolin can be explained by its mesoporous surface and acidity, which facilitated the cracking reaction.

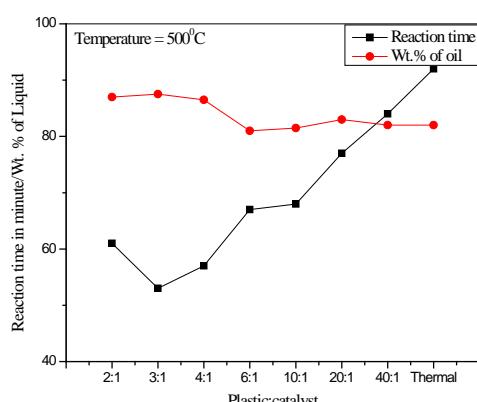


FIG. 4a EFFECT OF PLASTIC: CATALYST RATIO ON THE REACTION TIME AND OIL YIELD OF PYROLYSIS OF POLYPROPYLENE

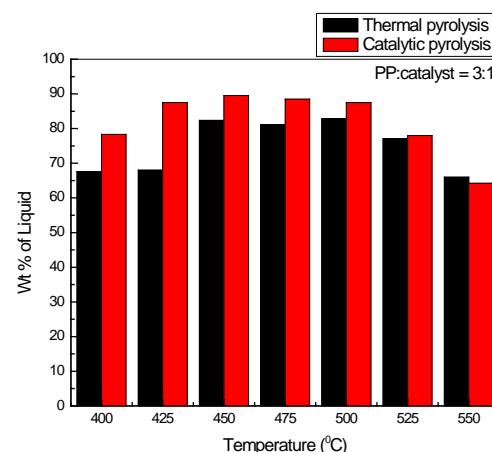


FIG. 4b EFFECT OF CATALYST ON OIL YIELD AT DIFFERENT TEMPERATURE

From Figure 5a, it is observed that the reaction time of the pyrolysis reaction also decreased with addition of catalyst. Figure 5b provides a comparison of the rate of production of oil in thermal and catalyzed pyrolysis. In thermal pyrolysis, there was gradual increase in oil production with time. Whereas there was sharp increase in oil yield with time observed in presence of the catalyst.

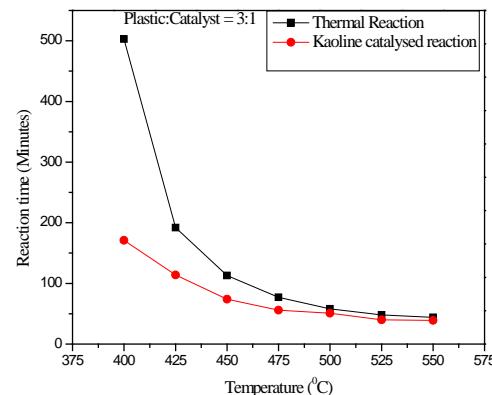


FIG. 5a EFFECT OF TEMPERATURE AND CATALYST ON REACTION TIME

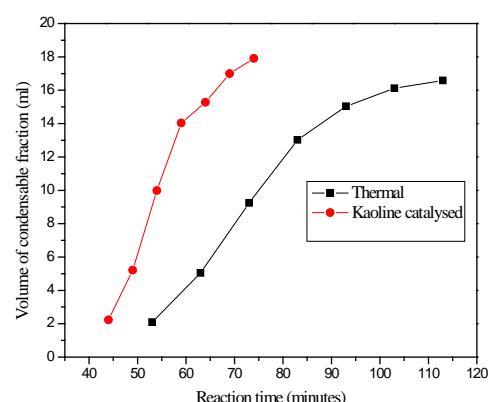


FIG. 5b EFFECT OF CATALYST ON RATE OF PRODUCTION OF OIL

A comparison of product distribution and basic physical properties of the oil obtained from thermal and catalytic pyrolysis of waste polypropylene is summarized in the Table 1. The density and viscosity of the oil obtained in the two processes show a remarkable difference.

Reusability of Catalyst

The activity of kaolin catalyst was studied by re-using it repeatedly in the degradation of polypropylene and the results are summarized in the Table 2. It is

observed that the yield and quality of liquid oil product remain almost same up to four times repeated use of the catalyst and yield decreased at 5th reuse. The reaction time of the reaction increased gradually for every repeated use.

The decrease in the catalytic activity may be due to the deposition of carbon and other plastics impurities over the surface. The SEM EDX (Figure 6 a b c d) of the catalyst sample clearly distinguishes the deposition of carbon over the surface of used catalyst.

TABLE 1 PYROLYSIS OF POLYPROPYLENE IN OPTIMUM CONDITION

Parameters	Type of pyrolysis reaction	
	Thermal (Temperature = 500 °C)	Kaolin catalysed (Plastic: catalyst = 3:1 and Temperature = 500 °C)
Liquid product (wt. %)	82.85	87.5
Gaseous/volatile(wt.%)	16.25	11.75
Solid residue (wt. %)	0.9	0.75
Density of oil at 15 °C (in g/cc)	0.84	0.745
Viscosity of oil at 30 °C (in Cst)	4.31	2.18

TABLE 2 PRODUCT DISTRIBUTION, REACTION TIME AND PHYSICAL PROPERTIES OF OIL OBTAINED IN CATALYTIC PYROLYSIS WITH FEED- WP-1:3 AT TEMPERATURE- 500 °C

No of times re-used	Weight of different fractions in weight %			Residence time in minutes	Specific gravity of oil @ 15 °C/15 °C	Viscosity of oil at 30°C in Cst
	Oil	Gas	Solid residue			
Fresh	89.5	8.9	1.6	44	0.7777	2.27
1 st time	87.5	10.6	1.9	58	0.7776	2.27
2 nd time	87.5	10.4	2.1	64	0.7645	2.27
3 rd time	88	10.25	1.75	68	0.7641	2.26
4 th time	88	10.4	1.6	68	0.7638	2.26
5 th time	84	14.25	1.75	73	0.7630	2.24
Regenerated catalyst	88	10.25	1.75	45	0.7732	2.26

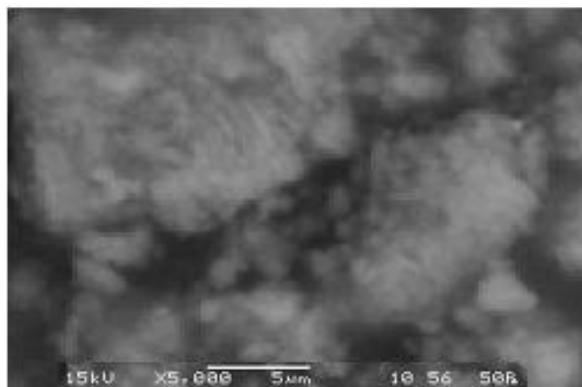


FIG. 6a SEM OF FRESH KAOLIN

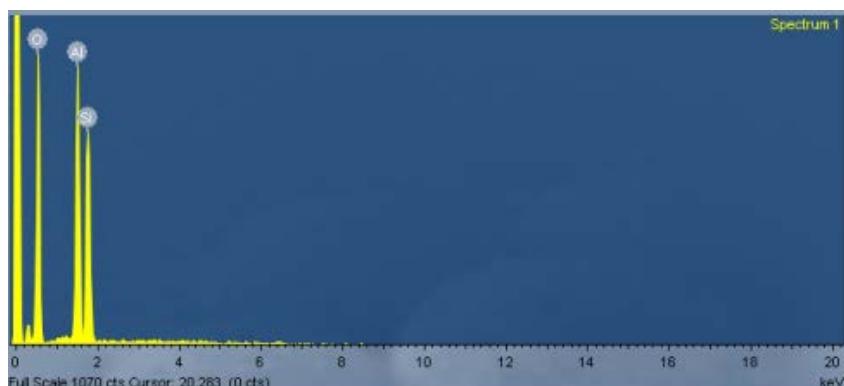


FIG. 6b EDX OF FRESH KAOLIN

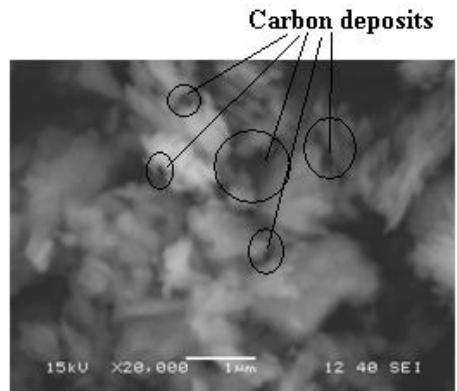


FIG. 6c SEM OF USED KAO LIN

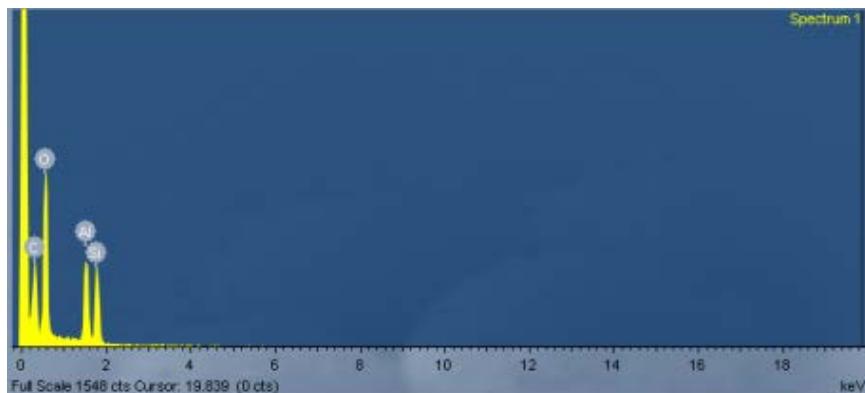


FIG. 6d EDX OF USED KAO LIN

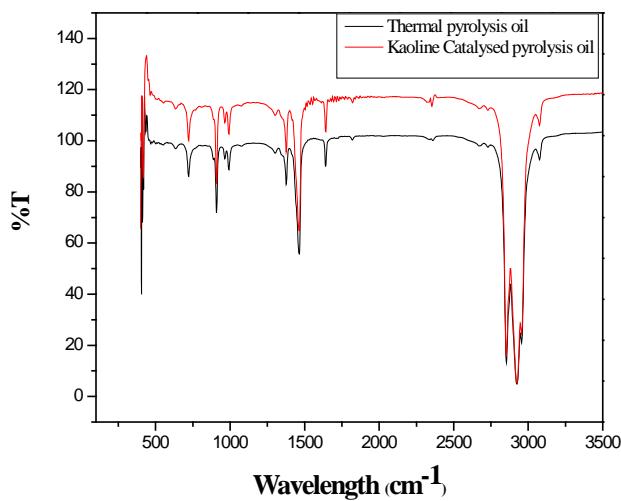


FIG. 7 FTIR OF OIL

The kaolin after usefor 5th run degradation was regenerated by calcinating it inside a muffle furnace at 750°C for one hour. The catalytic activity of regenerated catalyst was found to be almost same as that of the fresh kaolin. When the used catalysts were regenerated at high temperature, the deposited carbon burnt off and surface of catalyst become free of all depositions.

Characterization of Liquid Products

The oil sample was characterized using FTIR for functional group composition, GC-MS for detail composition and fuel properties to know its usability as an engine fuel. Figure 7 indicates the FTIR of thermal and catalytic pyrolysed oil at 500°C. The important assignments were summarized in Table 3.

TABLE 3 FTIR ASSIGNMENTS OF PYROLYSIS OIL

Wave number (cm ⁻¹)	Type of vibration	Nature of functional group
2956/2916	C-H stretching	Alkane
1377	C-H Scissoring and Bending	Alkane
2870	C-H stretching	Alkane
1651	C=C stretching	Alkene
1456	C=C stretching	alkene
970	C-H Bending	Alkene
887	C-H out of plane bending	Alkene
738	C-H Bending	Alkene, Phenyl ring substitution
1110, 1156	C-O stretching	Alcohols, Ethers, Carboxylic acids, Esters
1694, 1710, 1770	C=O stretching	Aldehydes, Ketones, Carboxylic acids, Esters

TABLE 4 GC-MS COMPOSITION OF OIL OBTAINED BY THE CATALYTIC PYROLYSIS OF POLYPROPYLENE AT 500°C

Peak	Retention Time In Minute	Area%	Molecular Formula
1	3.071	1.68	C ₁₂ H ₂₄
2	3.900	1.30	C ₁₀ H ₂₀
3	4.683	2.58	C ₁₁ H ₂₄
4	4.744	1.81	C ₁₀ H ₂₂
5	5.483	3.57	C ₁₂ H ₂₄
6	5.543	2.90	C ₁₂ H ₂₄
7	5.771	3.59	C ₁₂ H ₂₄
8	5.836	3.62	C ₁₄ H ₃₀ O
9	6.118	1.85	C ₁₂ H ₂₄
10	6.318	1.60	C ₁₂ H ₂₄
11	6.388	0.64	C ₁₀ H ₂₀ O
12	6.518	0.83	C ₁₂ H ₂₄
13	6.617	0.70	C ₁₃ H ₂₈ O
14	8.261	1.01	C ₁₀ H ₂₂ O
15	8.739	8.82	C ₁₂ H ₂₄
16	8.843	1.84	C ₁₁ H ₂₂
17	8.944	1.84	C ₁₂ H ₂₄
18	9.081	7.39	C ₁₁ H ₂₂
19	9.144	7.24	C ₁₃ H ₂₈ O
20	9.264	3.11	C ₁₃ H ₂₈ O
21	9.382	4.98	C ₁₁ H ₂₄ O
22	9.761	1.24	C ₁₂ H ₂₄
23	11.618	2.26	C ₁₂ H ₂₄
24	12.007	1.80	C ₁₃ H ₂₈ O
25	14.152	3.42	C ₁₂ H ₂₄
26	14.427	2.24	C ₁₂ H ₂₄
27	14.503	1.69	C ₁₂ H ₂₆ O
28	14.527	1.72	C ₁₂ H ₂₄
29	14.878	1.58	C ₁₂ H ₂₄
30	16.410	1.65	C ₁₈ H ₃₆
31	18.452	1.53	C ₁₈ H ₃₆
32	18.832	1.01	C ₁₂ H ₂₄
33	19.131	0.78	C ₁₂ H ₂₄
34	20.312	0.97	C ₁₈ H ₃₆
35	22.607	0.53	C ₁₈ H ₃₆
36	24.145	0.41	C ₁₈ H ₃₆

The GC-MS of the oil obtained in thermal and kaolin catalytic pyrolysis reaction at 500°C are shown in Figure 8.

Different components present in the oil obtained by comparing NIST library are summarized in the Table 4. This result indicates the presence of different hydrocarbons mostly alkanes and alkenes in the oil. In addition, some oxygenated compounds such as

alcohol, ketone, etc. are also found in the oil, which may be due to oxidative degradation of polypropylene in presence of limited quantity of oxygen inside the reactor as the reaction is not carried out in inert atmosphere.

Hayashi J et al. reported that polypropylene is more susceptible to oxidation than others because it contains

TABLE 5 FUEL PROPERTIES OF THE OIL OBTAINED AT 500 °C OBTAINED FROM KAOLIN CATALYSED PYROLYSIS

Tests	Test Protocol	pyrolysis oil
Colour	-----	Yellow
Specific Gravity@ 15°C/15 °C	I.S.1448: P.16	0.7777
Density @ 15 °C in gm/cc	I.S.1448: P.16	0.7771
Kinematic Viscosity in Cst@ 30 °C	I.S.1448:P: 25	2.27
Pour Point	I.S.1448: P:10	< - 45°C
Cloud Point	I.S.1448: P:10	< - 45°C
Gross calorific Value in Kcals/kg	I.S. 1448: P:6	11,256
Flash Point by Abel	I.S.1448: P:20	< - 12°C
Fire Point	I.S. 1448: P:20	< - 12°C
Boiling point range (°C)	I.S. 1448: P:18	68-346

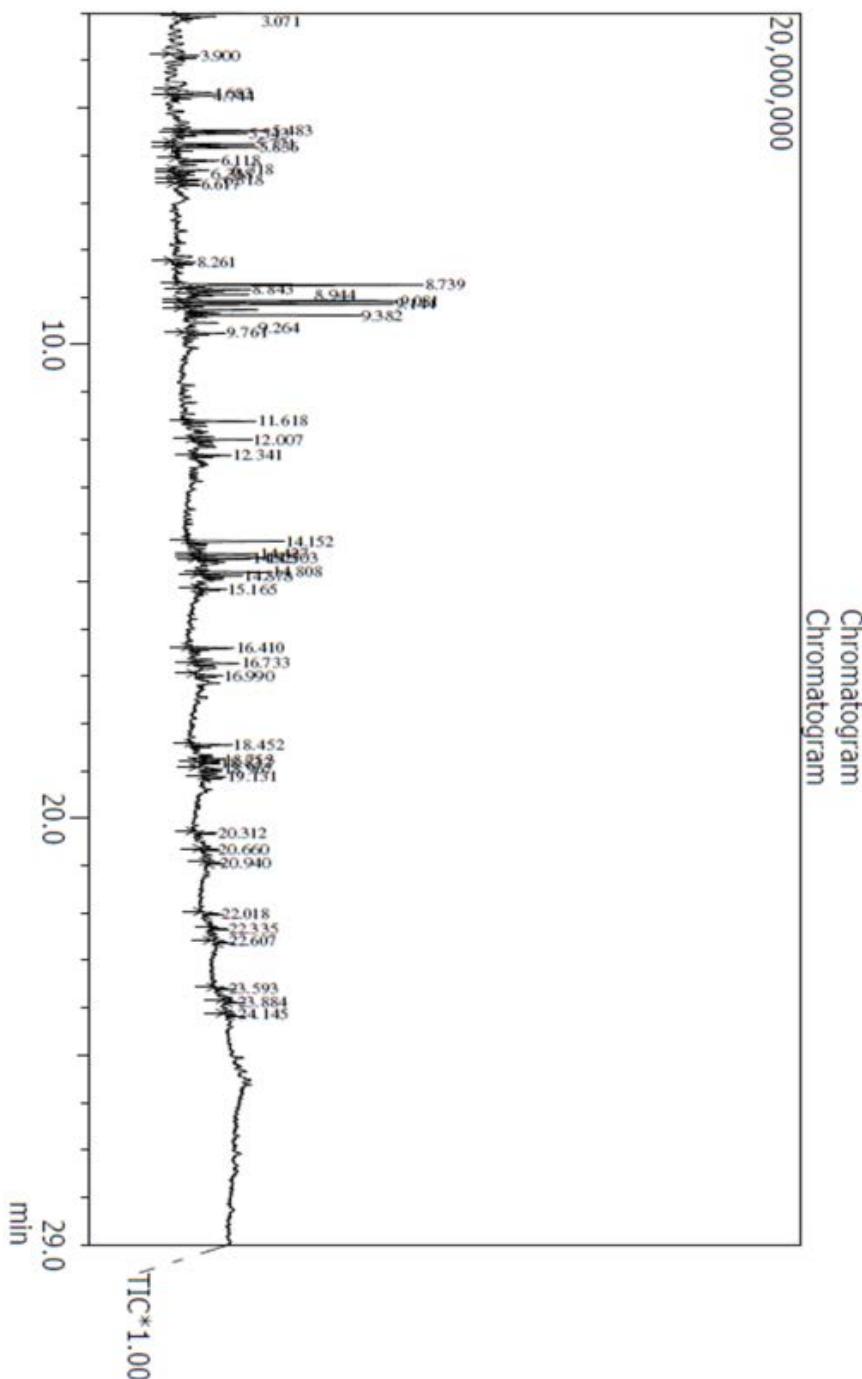


FIG. 8 GC-MS OF OIL OBTAINED IN THE CATALYTIC PYROLYSIS WITH 1:3 CATALYST TO POLYPROPYLENE FEED AT 500 °C

tertiary carbons and forms peroxide in the chemical form of $-C-O-O-H$ in presence of oxygen even at 150°C. Peroxides are further decomposed to more stable oxygen-containing groups such as hydroxyl and carbonyl groups [Hayash, Nakahara, and Kusakabe, Morooka, 1998].

All the fuel properties of the oil were tested by prescribed IS methods and the results are summarized in Table 5.

From the distillation report of the oil, it was observed that the boiling point range of the oil is 68-346°C using kaolin, which inferred the presence of mixture of different oil components such as gasoline, kerosene and diesel in the oil. Again, 30% oil recovery occurred at 160°C, which was the boiling range of gasoline, while the rest must be in the range of kerosene and diesel. All the other fuel properties of the oil obtained using the catalyst was almost similar and comparable to that of petro fuels. Based on this result, it can be concluded that the oil produced in the catalytic pyrolysis can be used as a substitute of petro fuels in engine.

Conclusion

The kaolin is found as an efficient catalyst for the conversion of waste polypropylene to gasoline/diesel/kerosene range chemicals. It increases the oil yield and the rate of pyrolytic reaction. In addition, the quality of oil produced from the kaolin catalysed pyrolysis reaction of polypropylene is better as compared to that produced from thermal pyrolysis. The maximum oil yield in the catalytic process is 87.5% with 3:1 plastics to catalyst feed at 500°C. In addition, it can be reused repeatedly without much affecting the oil quality. Again, the used catalyst can be regenerated and performance of the regenerated catalyst is found that same as that of the fresh kaolin. Natural kaolin being available abundantly could be a good candidate for its commercial application in the degradation of polypropylene. Further detailed kinetic studies would be necessary for a better understanding of the degradation mechanism and design of catalyst for proper uses of degraded products.

REFERENCES

Achilias, D.S., Roupakias, C., Megalokonomos, P., Lappas, A.A., Antonakou, E.V., "Chemical recycling of plastic wastes made from polyethylene (LDPE and HDPE) and polypropylene (PP)", Journal of Hazardous Materials, Vol.149, 2007, PP. 536–542.

- Aguado, J., Serrano, D.P., Romero, M.D., Escola, J.M., "Catalytic conversion of polyethylene into fuels over mesoporous MCM-41", Chemical Communications Vol. 6, 1996, PP. 725-732.
- Aguado, J., Sotelo, J., Serrano, D.P., Calles, J.A., Escola, J.M., "Catalytic conversion of polyolefins into liquid fuels over MCM-41: Comparison with ZSM-5 and amorphous SiO₂-Al₂O₃", Energy and Fuels, Vol.11, 1997, PP. 1225-1232.
- Audisio, G., Silvani, A., Beltrame, P.L., Carniti, P., "Catalytic thermal degradation of polymers : Degradation of polypropylene", Journal of Analytical and Applied Pyrolysis, Vol.7, 1984, PP. 83-90.
- Chaianansutcharit, S., Katsutath, R., Chaisuwan, A., Bhaskar, T., Nigo, A., Muto, A., "Catalytic degradation of polyolefins over hexagonal mesoporous silica: Effect of aluminum addition", Journal of Analytical and Applied Pyrolysis, Vol.80, 2007, PP. 360-368.
- Durmus, A., NaciKoc, S., SeldaPozan, G., Kasgoz, A., "Thermal-catalytic degradation kinetics of polypropylene over BEA, ZSM-5 and MOR zeolites", Applied Catalysis B, Vol. 61, 2005, PP. 316–322.
- Hayash, J., Nakahara, J., Kusakabe, K., Morooka, S., "Pyrolysis of polypropylene in the presence of oxygen", Fuel Processing Technology, Vol.55, No.3, 1998, PP>265-275.
- Hwang, E.Y., Choi, J.K., Kim, D.H., Park, D.W., Woo, H.C., "Catalytic degradation of polypropylene i. Screening of catalysts", Korean Journal of Chemical Engineering, Vol. 15, No.4, 1998, PP. 434-438.
- Ishihara, Y., Nanbu, H., Iwata, C., Ikemura, T., Takesue, T., "The Catalytic Degradation Reaction of Polypropylene with Silica-Alumina", Bulletin of Chemical Society Japan, Vol.62, 1989, PP. 2981-1988.
- Jung, S.H., Cho, M.H., Kang, B.S., Kim, J.S., "Pyrolysis of a fraction of waste polypropylene and polyethylene for the recovery of BTX aromatics using a fluidized bed reactor", Fuel Processing Technology, Vol. 91, 2010, PP. 277–284.
- Kim, J.R., Kim, Y.A., Yoon, J.H., Park, D.W., Woo, H.C., "Catalytic degradation of polypropylene: effect of dealumination of clinoptilolite catalyst", Polymer Degradation and Stability, Vol. 75, 2002, PP. 287-294.
- Lin, Y.H., Yen, H.Y., Fluidised bed pyrolysis of polypropylene over cracking catalysts for producing

- hydrocarbons, Polymer Degradation and Stability, Vol.89, 2005, PP. 101-108.
- Lin, Y.H.,Sharratt, P.N., Garforth, A.A., Dwyer,J., "Catalytic Conversion of Polyolefins to Chemicals and Fuels over Various Cracking Catalysts", Energy and Fuels, Vol.12, 1998, PP. 767-773.
- Marcilla, A., Go' mez, A., Reyes-Labarta, J.A., Giner,A., "Catalytic pyrolysis of polypropylene using MCM-41: kinetic model", Polymer Degradation and Stability, Vol.80, 2003, PP.233-240.
- Mordi, R.C., Fields, R., Dwyer, J., Thermolysis of low density polyethylene catalysed by zeolites", Journal of Analytical and Applied Pyrolysis, Vol.29, 1994, PP. 45-54.
- Mordi, R.C., Fields, R., Dwyer,J., "Gasoline range chemicals from zeolite-catalysed thermal degradation of polypropylene". Journal of the Chemical Society - Chemical Communications, Vol.4, 1992, PP. 374-381.
- Negelein, D.L., Lin, R., White,R.L., "Effects of catalyst acidity and structure on polymer cracking mechanisms", Journal of Applied Polymer Science, Vol.67, 1998, PP. 341-349.
- Panda, A.K., Singh, R.K., Mishra,D.K., "Thermolysis of waste plastics to liquid fuel: A suitable method for plastic waste management and manufacture of value added products—A world prospective", Renewable and Sustainable Energy Reviews, Vol 14, No 1, 2010, PP. 233-248.
- Panda, A.K., Mishra, D.K., Mishra, B.G., Singh, R.K., "Effect of Sulphuric acid treatment on the physicochemical characteristics of Kaolin clay", Colloids and Surfaces A: Physicochemical and Engineering Aspects, Vol.363, No.1-3, 2010, PP. 98-104.
- Panda, A.K., Singh, R.K., "Catalytic performances of kaoline and silica alumina in the thermal degradation of polypropylene", Journal of Fuel Chemistry and Technology, Vol. 39, No.3,2011, PP.198-202.
- Sakata, Y., Uddin, M.A., Koizumi, K., Murata, K., "Catalytic Degradation of Polypropylene into Liquid Hydrocarbons Using Silica-Alumina Catalyst" Chemical letters, Vol. 8, 1996, PP. 245-251.
- Salvador, C., Cardona, A., Corma,A., "Tertiary recycling of polypropylene by catalytic cracking in a semibatch stirred reactor Use of spent equilibrium FCC commercial catalyst", Applied Catalysis B, Vol.25, 2000, PP.151-162.
- Uddin, M.A., Koizumi, K., Murata, K., Sakata, Y., "Thermal and catalytic degradation of structurally different types of polyethylene into fuel oil", Polymer Degradation and Stability, Vol.56, 1997, PP. 37-44.
- Uddin, M.A., Sakata, Y., Muto, A., Shiragam, Y., Koizumi, K., Kanada,Y., "Catalytic degradation of polyethylene and polypropylene into liquid hydrocarbons with mesoporous silica", Microporous Materials, Vol.21, 1998, PP. 557-564.
- Zhao, W., Hasegawa, S., Fujita, J., Yoshii, F., Sasaki, T., Makuuchi,K., "Effect of irradiation on pyrolysis of polypropylene in the presence of zeolite". Polymer Degradation and Stability, Vol. 53,1996, PP. 199-206.
- Zhao, W., Hasegawa, S., Fujita, J., Yshii, F., Sasaki, T., Makuuchi,K., "Effects of zeolites on the pyrolysis Polypropylene", Polymer Degradation and Stability, Vol.53, 1996, PP.129-135.



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